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Technical Report

PREPARATION OF $K_3Co(CN)_5Br$ AND $K_3Co(CN)_5I$ BY AN ATOM TRANSFER REACTION

by

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Abstract

The new compounds $K_3Co(CN)_5Br$ and $K_3Co(CN)_5I$ are described. They were prepared by the reaction

$$2Co(CN)_5^{-3} + X_2 = 2Co(CN)_5X$$

which appears to be a bona fida example of an atom transfer oxidation process. A possible mechanism for the reaction is suggested, and an explanation of why it takes place with aqueous bromine and triiodide ion but not with chlorine.

Introduction

It is well known that transition metals form rather stable complex cyanides of the type $K_nM(CN)_6$, where M may be V(II),[1] (III),[2] (IV),[3] Cr(II),[4] III,[4] Mn(I),[5]

(1) F. Ephraim, "Inorganic Chemistry," Gurney and Jackson, London, 1942, p. 277 5th Edition.
(2) J. N. Friend, "Textbook of Inorganic Chemistry," C. Griffin and Co., London, 1922, Vol. VI, part 3, p. 105.
(3) A. Yakimach, Compt. rend. 191, 789 (1930).
(4) L. Pauling, "Nature of the Chemical Bond," Cornell University Press, 1940.
(5) W. Manchot and H. Gall, Ber., 61(B), 1135 (1928).

(II),[4] (III),[4] Fe(II),[4] (III),[4] Ru(II),[6] (III),[6] and Co(III).[4] Most of these

(6) D. DeFord, Abstracts of April 1950 meeting of American Chemical Society at Detroit.

complexes are quite stable, and those of iron and cobalt are exceptionally so; thus decomposition of the Co(III) complex is effected only by prolonged heating with concentrated sulfuric acid. There is, in addition, a series in the iron family of the type $K_2Fe(CN)_5(R)$,[7] where R may be CO, NO, NH_3, H_2O,

(7) H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1944.

or SCN,[8] but not a halogen ion. Beyond this, however, there is a very limited

(8) R. Brunner, Z. anorg. allgem. Chem., 190, 384 (1930).

number of mixed cyanocomplexes. Probably various stages of aquocyano complex formation exist for all the hexacyanides, as evidenced, for example, by the exchange kinetics of radiocyanide ion with the various hexacyanides,[9] but only

(9) A. W. Adamson, J. P. Welker and W. B. Wright, T. Am. Chem. Soc. 73, 4786 (1951).

the following have been isolated: $K_3Fe(CN)_5(H_2O)$,[10] $K_2Co(CN)_5(H_2O)$,[11,12] and

(10) S. Jimori, Z. anorg. chem., 167, 145 (1927).
(11) P. R. Ray, J. Ind. Chem. Soc., 1927, 327
(12) P. R. Ray and N. K. Dutt, Z. anorg. allgem. Chem., 234, 65 (1937).

$KCo(CN)_4(H_2O)_2$.[13] Finally, the existence in aqueous solution of $K_3Co(CN)_4(OH)_2$[14]

(13) P. R. Roy and T. Guptuchanduri, ibid, 220, 154 (1934).
(14) L. C. Smith, J. Kleinberg, and E. Griswald, J. Am. Chem. Soc. 75, 449 (1953).

has been claimed. The lack of a complete nitropruside type series of Co(III) complexes may simply reflect insufficient effort on the part of investigators; thus the species $K_4Co_2(CN)_9NO_2$ has been reported,[15] although attempts to prepare

(15) A. Rosenheim and I. Kappel, Z. anorg. allgem. Chem., 17, 35, 67 (1898).

$KCo(CN)_5(NO)$ and $K_2Co(CN)_5(NO)$ have been unsuccessful.[16]

(16) A. A. Blanchard and F. S. Magnusson, J. Am. Chem. Soc., 63, 2236 (1941).

As is evident from the above brief review, one type of complex that is noticeable by its absence is the mixed halogenocyano one. The present report covers work done in this Laboratory demonstrating the existence of the solids $K_3Co(CN)_5Br$ and $K_3Co(CN)_5I$, and introduces an interesting method for their preparation.

Results and Discussion

Preparation of $K_3Co(CN)_5Br$ from $[Co(NH_3)_5Br](NO_3)_2$. The first attempts to prepare $K_3Co(CN)_5Br$ were made in connection with some earlier work in this Laboratory.[17] It was first found that treatment of $K_2Co(CN)_5(H_2O)$, prepared

(17) A. W. Adamson and J. M. Grunlund, ibid., 73, 5508 (1951).

by the method of Ray,[11,12] with HBr or KBr in aqueous solution did not yield any new product. It was therefor concluded that if $Co(CN)_5Br^{-3}$ existed, its aquation equilibration was very unfavorable.

The bromopentacyanide was successfully synthesized, however, by a rather roundabout method. One of the intermediate steps in the preparation of the

aquo complex involves a reaction between thiosulfatopentamminocobalt(III) chloride and strong potassium cyanide solution, to form potassium thiosulfatopentacyanocobalt(III). This rather unusual reaction was made use of in a successful synthesis of the bromopentacyano complex. To an aqueous solution of twenty four grams of potassium cyanide, twenty one grams of bromophenamminecobalt(III) were added. A dark reddish yellow solution resulted, from which ammonia is evolved. Addition of alcohol to about 75% by volume gave a voluminous cream colored precipitate which was filtered off, washed with alcohol and ehter, and dried in a vacuum desiccator.

The above product was analysed for potassium by the chloro platinate method,[18] for cobalt by the alpha nitroso beta naphthol method[19] (after evaporation with hydrochloric acid to decompose the complex), and for bromide by a method due to Kamm.[20] One quarter of a gram of the complex was refluxed with thirty five cc of absolute alcohol and 3.5 grams of metallic sodium were added gradually. After about two hours, the solution was cooled, and fifty cc of water added. The solution was then acidified with nitric acid and the bromide present was determined by the Volhard method. The results of the analyses are summarized in Table I.

(18) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Analysis," The MacMillan Co., 1936, p. 390.
(19) I. M. Kolthoff and E. B. Sandell, ibid, p. 77.
(20) O. Kamm, "Qualitative Organic Analysis," J. Wiley and Sons, Inc., 2nd Ed., p. 199.

Table I

Analysis of Potassium bromopentacyanocobalt(III)

	Experimental		Theoretical I	Theoretical II
Br	19.44 19.34	19.39	20.69	19.39
Co	15.59 15.91 15.73	15.74	15.26	15.60
K	29.78 31.15 30.47 30.81	30.55	30.37	30.18

I. Calculated for $K_3Co(CN)_5Br$. II. Calculated, assuming 6.3% $K_2Co(CN)_5(H_2O)$ impurity.

Preparation of $K_3Co(CN)_5Br$ and $K_3Co(CN)_5I$. The second synthetic method to be described is based on the entirely different approach indicated by the type reaction:

$$2Co(CN)_5^{-3} + X_2 = 2Co(CN)_5X^{-3} \qquad (1)$$

Although the complex formed between Co(II) and cyanide ion (ordinarily prepared as the deep violet crystals of the potassium salt) was for some seventy years repeatedly referred to as $Co(CN)_6^{-4}$, work in this Laboratory had shown the potassium salt to be $K_3Co(CN)_5$.[21] This was considered to be a striking indication of the reluctance of Co(II) to exceed the Kr structure in forming a covalently bonded complex. The ion $Co(CN)_5^{-3}$ is a powerful reducing agent in aqueous media; it is rapidly oxidized by atmospheric oxygen, and will slowly reduce water[14,22]. Smith[14] et al have recently supplied evidence that one of the final products of the air oxidation is $Co(CN)_4(OH)_2^{-3}$, but it seems fairly definite that the first product is $Co(CN)_5(H_2O)^{-2}$.[23]

(21) A. W. Adamson, J. Am. Chem. Soc., 73, 5710 (1951).

(22) R. A. Ogg, Abstracts of American Chemical Society meeting, March 1953, Los Angeles.

(23) D. N. Hume and I. M. Kolthoff, J. Am. Chem. Soc., 71, 876 (1949).

The study of the reaction of $Co(CN)_5^{-3}$ with halogens was first undertaken here with the object of ascertaining if possible whether the oxidation proceeded by an electron transfer mechanism or whether an atom transfer process was also possible. The two possibilities are exemplified by the following reactions.

Electron Transfer:

$$Co(CN)_5^{-3} + X_2 = Co(CN)_5^{-2} + X_2^- \quad (2)$$

$$Co(CN)_5^{-3} + X_2^- = Co(CN)_5^{-2} + 2X^-$$

$$Co(CN)_5^{-2} + H_2O = Co(CN)_5(H_2O)^{-2}$$

Atom Transfer:

$$Co(CN)_5^{-3} + X_2 \text{ (or } X_3^-) = Co(CN)_5X^{-3} + X \text{ (or } X_2^-) \quad (3)$$

$$Co(CN)_5^{-3} + X \text{ (or } X_2^-) = Co(CN)_5X^{-3} (+ X^-)$$

The oxidation by water and by oxygen is not easily identified as to type, but it was considered that the nature of the product upon oxidation by a halogen should permit a decision. If an electron transfer process occured, the immediate product, $Co(CN)_5^{-2}$ should aquate to form $Co(CN)_5(H_2O)^{-2}$ rather than add X^-, in view of the observation that the reaction

$$Co(CN)_5(H_2O)^{-2} + Br^- = Co(CN)_5Br^{-3} + H_2O \quad (4)$$

did not occur, plus our own observation that the aquation rate of the bromopentacyano complex was noticeably rapid. Moreover, air oxidation of $Co(CN)_5^{-3}$ in the presence of concentrated chloride or bromide yielded only $Co(CN)_5(H_2O)^{-3}$, another indication that no species of unusual reactivity toward halide ion were present during the oxidation process.

On the other hand, if an atom transfer mechanism prevailed, the sequence of the type illustrated by (3) should occur, and the product should be the halogenopentacyanide rather than the aquo pentacyanide.

The results obtained are as follows. The procedure consisted of preparing a solution of 20 gms of cobaltous nitrate hexahydrate in 150 cc of water, which was deaerated by bubbling nitrogen through it, and cooled in an ice bath to ca. 5°C. Solid potassium cyanide was then added slowly in amount corresponding to give cyanides per cobalt plus a slight excess sufficient to yield a clear solution. This solution of $Co(CN)_5^{-3}$ as then added rapidly to one contained an excess of bromine or of potassium triiodide, and the product isolated by the addition of sufficient alcohol to cause precipitation. The product was reprecipitated, washed with alcohol and ether and dried.

With bromine as the oxidant the product was identical to that obtained by the syntheses for $K_3Co(CN)_5Br$ described above, namely a light brown, highly soluble powder. In this case, the cobalt analysis was made by the method of Cartledge and Nickols,[24] that for potassium by a flame spectrophotometer,

(24) G. H. Cartledge and P. M. Nickols, Ind. Eng. Chem., Anal. Ed., 13, 20 (1941).

and that for bromide as before. The results were as follows. Potassium analysis: found 28.5%, calc. for $K_3Co(CN)_5Br$, 30.3; cobalt, found 15.8, calc., 15.3; bromide, found 21.7, calc. 20.7. The analyses indicate the presence of an impurity such as $CoBr_2$, but no satisfactory way was found to purify the complex further. It was too soluble to be recrystallized from aqueous solution, and no other solvent could be found.

With potassium triiodide as the oxidant, the procedure was the same, and the product obtained was dark reddish brown in color. Analyses were by the same procedures as above with the following results. Potassium, found 25.9%, calc. for $K_3Co(CN)_5I$, 27.3; cobalt, found 14.0, calc. 13.6; iodide, found 29.8, calc. 29.3.

The course of the reaction with aqueous chlorine appeared to be entirely different, however. Following the above procedure, a light colored product was isolated, but contained half or less of the theoretical amount of chloride, although the potassium and cobalt analyses were close to the theoretical value. However, the formula weights of CN^-, and Cl^- are sufficiently close together that potassium and cobalt analyses do not permit easy distinction between $K_3Co(CN)_6$ and $K_3Co(CN)_5Cl$.

It is noteworthy that in all three cases above, it was important that the solution of $Co(CN)_5^{-3}$ be added <u>to</u> one containing <u>excess</u> halogen. If excess of the Co(II) complex was present, either through reversing the order of addition, or because of insufficient halogen being present, variable amounts of a water insoluble ocre colored product were obtained. This appeared to be some type of polymeric cobalt cyanide since it dissolved in excess potassium cyanide to give a solution the same color as that of $K_3Co(CN)_5$. This ocre product may have resulted from a reaction between $Co(CN)_5^{-3}$ and $Co(CN)_5Br^{-3}$ in which $Co(CN)_6^{-3}$ was the other product. Another complication occured with aqueous Cl_2 as the oxidant; if a large excess was employed, a black polymeric product resulted, apparently from the oxidation of cyanide by chlorine.

If reactions (3) represent the sequence with aqueous bromine as the oxidant, a possible explanation of the different behavior of aqueous chlorine would be that higher bond energy of Cl_2 makes the first step endoergic. Thus

$Cl_2(g) = 2Cl\ (g) \qquad \Delta F^\circ = 50$ Kcal

$Br_2(g) = 2Br\ (g) \qquad \Delta F^\circ = 33$ Kcal

In conclusion it should be noted that Taube has claimed that the redox reaction

$$Cr^{++} + Co(NH_3)_5Cl^{++} = Cr(H_2O)_5Cl^{++} + Co(II)\ (aq).$$

procedes by transfer of a Cl atom. Although his evidence is clear that the Cl ion transfers from Co to Cr during the reaction, it is still possible that the redox change occurs by charge (electron) transfer. The immediate product of a charge transfer would be a nascent Cr(III) ion which would be filling its covalently bound coordination sphere, and the species $[Co(NH_3)_5]^+$, which now being ionically bonded, would make it groups readily available to the adjacent Cr(III). Since Cr^{++} would tend to approach the $Cr(NH_3)_5Cl^{++}$ ion from the Cl^- side, just from electrostatic considerations, the Cl^- freed as a result of a charge transfer should all the more readily be picked up by the nascent Cr III. No such ambiguity in interpretation seems possible in the case of the reactions reported here; the halogen atom enters the coordination sphere and oxidizes the $Co(CN)_5^{-3}$ in one step. Finally, it should be mentioned that this type of process finds at least one precedent in the report by Schwarzenbach[25] that on

(25) G. Schwarzenbach, Helv. Chim. Acts, 32, 839 (1949).

treatment of the complex CoY^- (Y denoting the ethylenediaminetetracetate ligand) by aqueous bromine, the product $CoYBr^{-2}$ results (a coordinately bound Br displacing one of the carboxyl groups), whereas with other oxidants the expected electron transfer product CoY^- is obtained.